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Ultrafast dynamics of excitons in semiconductor quantum dots on a plasmonically active nano-structured silver film

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Abstract

The excited state dynamics of core–shell type semiconductor quantum dots (QDs) of various sizes in close contact with a plasmonically active silver thin film has been demonstrated by using picosecond resolved fluorescence spectroscopy. The non-radiative energy transfer from the QDs to the metal surface is found to be of Förster resonance energy transfer (FRET) type rather than the widely expected nano-surface energy transfer (NSET) type. The slower rate of energy transfer processes compared to that of the electron transfer from the excited QDs to an organic molecule benzoquinone reveals an insignificant possibility of charge migration from the QDs to the metallic film.

S Online supplementary data available from stacks.iop.org/Nano/22/195704/mmedia

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Control over the emitting property of a photon source is of much interest to a wide range of scientists ranging from physicists, chemists to biologists [1]. This control is essential for various potential applications including miniature lasers, light emitting diodes, single photon sources, solar energy harvesting, optical switches, optical sensors, etc [1–4]. The use of metallic surfaces for the control of the excitonic state of a photon emitter is evidenced in the literature [5, 6]. These studies exploit the reflecting properties of metal surfaces to control the local density of states (LDOS) of the photon emitter in proximity (at least 10 nm apart) [7] and carefully avoid direct contact with the metal surfaces [7] in order to disregard non-radiative energy transfer [7, 8]. Inevitably, direct contact of a photon source with a metal film brings complexity owing to the potential possibility, due to interference, of energy/charge transfer and excitonic coupling to the surface plasmon of the metallic surface [9, 10]. Although direct contact of the photon sources with metallic thin film is almost unavoidable for the realization of several photonic devices, including plasmonically coupled single photon transistors [11], there are few detailed systematic studies of the excitonic dynamics of photon sources in contact with plasmonically active metal film [9]. In a recent study, the dynamical consequence of the emission from CdSe quantum dots (QDs) on a gold thin film was demonstrated [9]. Using nanosecond resolved fluorescence spectroscopy, the study concluded the emission quenching to be non-radiative in nature. However, a detailed picture of the non-radiative energy transfer of the QDs and conclusive evidence to rule out charge transfer processes from the QDs to the gold thin film is lacking in the study.

In the present study, we have used CdSe/ZnS core–shell type semiconductor QDs of various sizes and a thin silver film (thickness 35 nm) as the model photon source and metallic surface, respectively. Using a high resolution transmission electron microscope (HRTEM) we have characterized the QDs. An atomic force microscope (AFM) and field emission gun scanning electron microscope (FEG-SEM) were used to study

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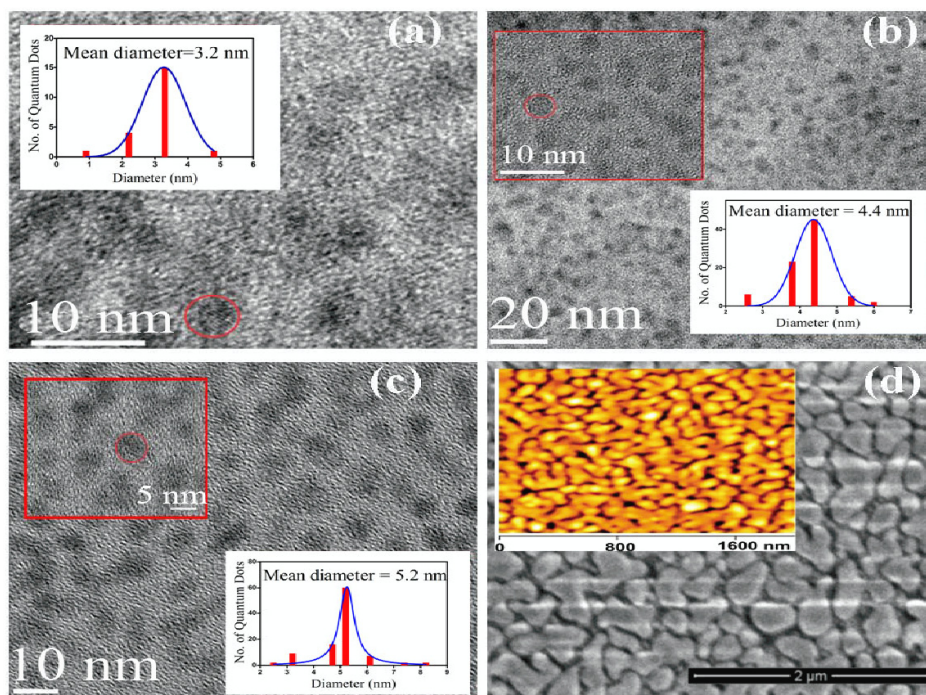
Figure 1. (a)–(c) HRTEM images of the QDs LBP, AG and BY, respectively. (d) SEM and AFM (inset) images of the silver film.

the nano-structured silver thin film on a quartz substrate. Picosecond resolved fluorescence spectroscopy on the QDs in contact with the silver film explores the dynamics of excitons. Our studies also explore the type of excitonic energy transfer and the possibility of photo-induced charge migration from the QDs to the metal film. Nano-surface energy transfer (NSET) [12], one of the other prevailing pathway of non-radiative quenching, was conclusively found to not to occur in this context.

2. Materials and methods

A thin film of silver (99.999%, 35 nm thick) was deposited on a quartz substrate using a vapour deposition technique and characterized by FEG-SEM (FEI, Helios 600), AFM (Vicco, CP-II) and a UV–vis spectrophotometer (Shimadzu). CdSe/ZnS core–shell QDs of various sizes (different emission maxima; λ_{max}^{em}) were purchased from Evident Technology. Three QDs, namely Lake Placid Blue (LPB; $\lambda_{max}^{em} = 490$ nm), Adirondack Green (AG; $\lambda_{max}^{em} = 528$ nm), and Birch Yellow (BY; $\lambda_{max}^{em} = 576$ nm), were characterized by HRTEM (FEI; Tecnai S-twin). Photoluminescence (PL) of the spin coated QDs and a QD–benzoquinone (BQ; Alfa Aesar) mixture on the silver film were measured using a Life-spec Spectrometer (Edinburgh Instruments, UK). All spectroscopic measurements were performed at room temperature. The excitation at 375 nm (IRF = 70 ps) was obtained using a pulsed laser diode. The excitation was vertically polarized, and the emission was recorded through a polarizer oriented at 55° from the vertical position. A long-pass filter at 420 nm was used in the collection path to effectively eliminate the possible scattered excitation.

3. Results and discussions

HRTEM images (figures 1(a)–(c)) reveal the diameters of the QDs to be 3.2 nm, 4.4 nm and 5.2 nm for LBP, AG and BY, respectively. The existence of the fringes ensures the high crystalline nature of the QDs. The SEM (figure 1(d)) and the AFM (inset of figure 1(d)) images of the silver film show that it is formed by the accumulation of silver particles of various sizes ranging from microns to nanometres. The absorption band maxima of the silver thin film at 440 nm (figure 2) is consistent with the presence of silver particles of diameter 10–30 nm in the thin film [13], which makes the film plasmonically active. Noble metal films having nano-structure exhibit one very interesting phenomenon known as localized surface plasmon resonance (LSPR) [14, 15] which arises from resonant oscillation of their free electrons in the presence of light. While the locations and PL peaks of the QDs on the thin film are schematically demonstrated in figure 2, the consequences of the excitonic dynamics of the QDs are evident in figure 3. Each PL decay curve was fitted by a multi-exponential to achieve lifetimes under various conditions. Table 1 shows the detailed time resolved lifetimes of the QDs. It is clearly evident from figure 3 and table 1 that the PL dynamics of QDs become significantly faster on the metal film compared to that on the quartz surface, which could be a consequence of either non-radiative energy transfer [9] or photo-induced charge transfer [16] to the host film. From the figure 3 and table 1 it is also evident that QDs in the presence of BQ offer much faster PL dynamics than those on the metal film. Strong lifetime quenching of QDs in the presence of BQ is a typical example of excited state interfacial charge migration from QDs to BQ, the well-known electron shuttle
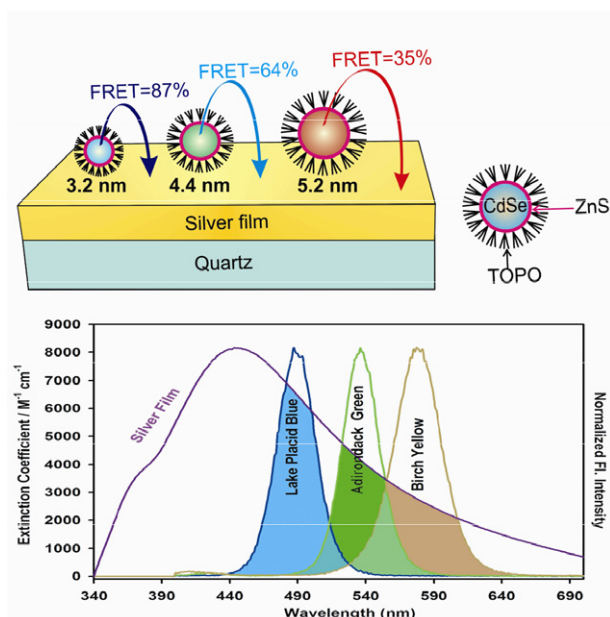
Figure 2. Schematic diagram of FRET from QDs to silver film (above). Overlap of the silver absorption with QD emission (below).

which pumps the excited electron out from semiconductor conduction band [16–18].

Figure 3 shows the picosecond resolved PL spectra of the QDs LPB, AG and BY under different conditions. The PL spectra were collected at the emission maximum of respective QDs. From the significant difference of the timescales of PL quenching of the QDs on the film from those in the QD–BQ complexes (table 1 and figure 3), we

conclude that the quenching phenomenon is attributable solely to energy transfer. The insignificantly smaller possibility of electron transfer from the QDs to the metal surface can be justified from the formation of a Schottky barrier [19] in the semiconductor metal junction (see supporting information available at stacks.iop.org/Nano/22/195704/mmedia). The equilibrium contact potential V_0, which is the order of 0.26 eV, is sufficiently higher to prevent the net electron transfer from semiconductor conduction band to metal side. As demonstrated earlier, ZnS shells around the CdSe QDs are not supposed to be a barrier to charge migration [16, 20, 21].

The non-radiative energy transfer is further justified by the strong spectral overlap between the QD emission with the LSPR band of the silver film (figure 2). Considering the energy transfer to be of the Förster resonance energy transfer (FRET) type, the efficiency of energy transfer depends on the inverse of the sixth power of donor–acceptor separation (see supporting information available at stacks.iop.org/Nano/22/195704/mmedia), $E = 1 - \frac{\tau_{DA}}{\tau_D}$, where τ_{DA} and τ_D are the excited state lifetime of the donor (QDs) in the presence of an acceptor (silver film) and the excited state lifetime of the donor in the absence of any acceptor (QDs on quartz substrate), respectively. The efficiency of FRET for the various QDs on the metal film is depicted in figure 2 and table 1 and found to be in excellent agreement with the estimated values. Both degree of overlap and distance between donor and acceptor have been accounted for simultaneously for FRET efficiency estimation. The FRET efficiency goes on decreasing from LPB to BY with increase in donor–acceptor distance. The effective donor–acceptor distances, which are the distances [22] from the centre of the QDs to the contact point of the QDs to the film,
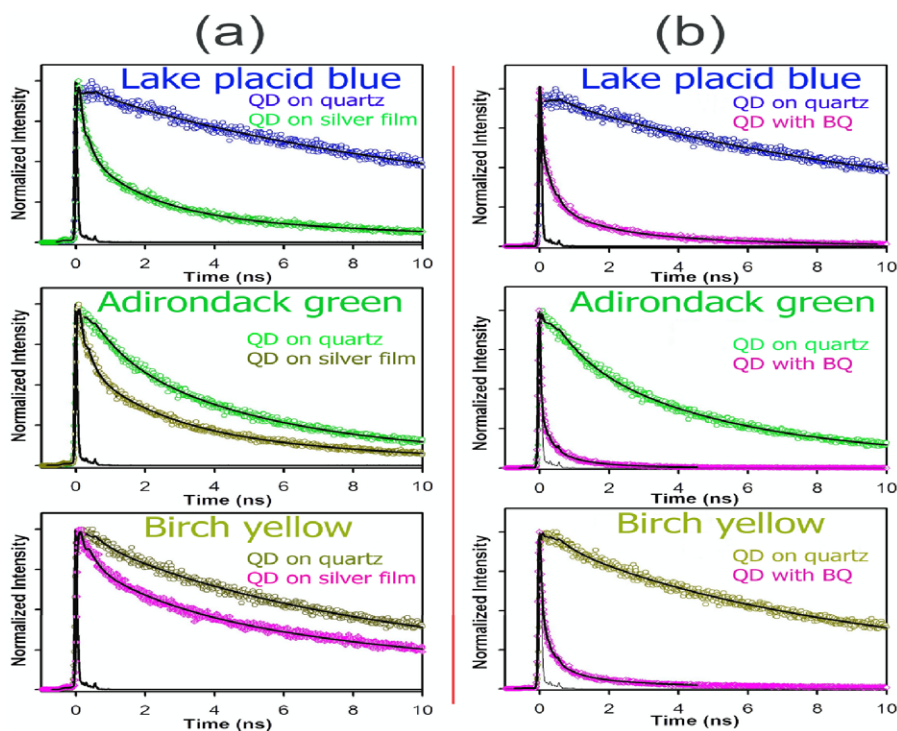

Figure 3. Picosecond resolved photoluminescence transients of QDs under various conditions. (a) Lifetime quenching of QDs by silver film due to energy transfer. (b) Lifetime quenching of QDs in the presence of BQ due to electron transfer.

Table 1. Individual (τ_i) and average (τ_{av}) fluorescence lifetimes of QDs in different conditions along with Förster distances (R_0), overlap integral ($J(\lambda)$), observed (FRET$_{EXP}$) and calculated (FRET$_{CAL}$) FRET efficiencies.

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	τ_{av} (ns)	R_0 (nm)	$J(\lambda) \times 10^{14}$ (M^{-1} cm^{-1} nm^4)	FRET$_{EXP}$	FRET$_{CAL}$
QD(LPB; 3.2 nm)	0.15(26%)	4.08(11%)	18.20(63%)	12				
QD-silver	0.15(64%)	1.72(24%)	8.60(12%)	1.54	3.6	3.67	87%	89%
QD-BQ	0.07(79%)	0.70(15%)	4.15(06%)	0.41				
QD(AG; 4.4 nm)	0.29(27%)	2.89(27%)	9.74(46%)	5.29				
QD-silver	0.18(59%)	2.20(26%)	8.10(15%)	1.90	3.56	3.41	64%	64%
QD-BQ	0.03(94%)	0.88(06%)		0.08				
QD(BY; 5.2 nm)	0.17(29%)	3.74(19%)	15.20(52%)	8.63				
QD-silver	0.13(36%)	0.87(22%)	11.00(42%)	4.80	3.5	3.06	35%	36%
QD-BQ	0.06(86%)	0.57(12%)	4.34(02%)	0.23				

are consistent with the estimated distances from the diameter of the QDs and the length of the capping ligand TOPO (0.8–1 nm) [23]. The details of the FRET calculations are given in the supporting information (available at stacks.iop.org/Nano/22/195704/mmedia).

Considering the fact that a point dipole (QDs here) can interact with an infinite metal surface, which is very relevant to our experiment, the energy transfer mechanism can be extended over the well-known FRET model as described above. The extended model was first introduced by Perssons and Lang [24] and is popularly known as nano-surface energy transfer (NSET) where the energy transfer efficiency depends on the inverse of the fourth power of donor–acceptor separation. The rate of NSET [12] $k_{NSET} = (\frac{1}{\tau_D})(\frac{d_0}{r})^4$, where τ_D is the donor lifetime and r represents the centre to centre separation between donor and acceptor species. The characteristic distance [12] $d_0 = (0.525 \times \frac{c^3 \Phi_D}{\omega^2 \omega_f \kappa_f})^{\frac{1}{4}}$, where Φ_D is the quantum efficiency, c is the velocity of light, ω is the frequency of donor electronic transition, ω_f is the Fermi frequency of metal and κ_f is the Fermi wavevector of the metal [12]. The calculated donor–acceptor distance (see supporting information available at stacks.iop.org/Nano/22/195704/mmedia), assuming that NSET is guiding the quenching process, was also found to be in micron range which is absolutely invalid in the present context.

4. Conclusion

In summary, our study essentially demonstrates the excited state exciton dynamics of QDs of various sizes in contact with plasmonically active of silver film. The nano-structure on the film surface is found to be responsible for the localized surface plasmon resonance (LSPR) of the metal film. Here we have accounted for every single aspect of the possible mechanisms of the quenching phenomenon (namely charge transfer, nano-surface energy transfer and Förster energy transfer). Among the various possibilities, it is clearly shown that only the non-radiative energy transfer process in the excited QDs takes part in the lifetime quenching and a simple FRET model is good enough to rationalize the quenching phenomenon. Though charge migration from the QDs to silver film is expected, it is not realized in our case due to the formation of a Schottky barrier.

Acknowledgments

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